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METHOD FOR THE MANUFACTURE OF A RAW MATERIAL POWDER FOR  
ELECTRONIC CERAMICS

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### Abstract

#### Objective

To provide a method for the manufacture of raw material powder for electronic ceramics.

#### Constitution

A method for the manufacture of a raw material powder for electronic ceramics characterized by the fact that a heated solution obtained by the dispersion of seed particles of a composite perovskite compound of the general formula  $ABO_3$  (first solution), a heated solution of a hydroxide of A (second solution), a heated solution of a base (third solution), and a solution of an alkoxide or an organic metal compound of B (fourth solution) are fed at specific ratios from separate paths to a static stirring-mixing apparatus having no moving parts, and contacting and stirring-mixing of the previously mentioned various solutions are carried out to the confluence point, at which said solutions are fed to the previously mentioned static stirring-mixing apparatus, to obtain a composite perovskite compound powder shown by the general formula  $ABO_3$ .

#### Effects

A raw material powder for electronic ceramics that has a grain size larger than the seed particles, has extremely well distributed particle diameters, has a high surface activity, and has good sintering characteristics can be manufactured at a low cost in an efficient manner.

### Claims

1. A method for the manufacture of a raw material powder for electronic ceramics characterized by the fact that a heated solution obtained by the dispersion of seed particles of a composite perovskite compound of the general formula  $ABO_3$  (in this formula, A is at least one metal element selected from divalent alkaline-earth metals, and B is at least one metal element selected from tetravalent metal elements) (first solution), a heated solution of the hydroxide of the alkaline-earth metal constituting A (second solution), a heated solution of a base (third solution), and a solution of an alkoxide of the metal element constituting B or a hydrolyzable organic metal compound selected from the elements constituting B (fourth solution) are fed at specific molar ratios from separate paths to a static stirring-mixing apparatus having no moving parts, and contacting and stirring-mixing of the previously mentioned first, second, third and fourth solutions are carried out to the confluence point, at which said solutions are fed to the

previously mentioned static stirring-mixing apparatus, to obtain a composite perovskite compound powder shown by the general formula  $ABO_3$  (the various symbols in this formula have the same definitions as those given previously).

2. The manufacturing method described in Claim 1, in which A is at least one metal element selected from the group consisting of barium, calcium, strontium, and magnesium.

3. The manufacturing method described in Claim 1, in which B is at least one metal element selected from the group consisting of titanium, zirconium and tin.

4. The manufacturing method described in Claim 1, in which the base of the third solution is sodium hydroxide, potassium hydroxide, lithium hydroxide, ammonium hydroxide, or an organic amine, or a mixture of these.

5. The method described in Claim 1, in which the solutions fed to the static stirring-mixing apparatus in a molar ratio of  $A:B:base = 1:1:(1-4)$ .

6. A method for the manufacture of a raw material powder for electronic ceramics characterized by the fact that the first, second, third and fourth solutions described in Claim 1, as well as a solution of an alkoxide or a hydrolyzable organic metal compound containing a metal element required for semiconductor formation (fifth solution), are fed separately to a static stirring-mixing apparatus having no moving parts to carry out the primary reaction for the formation of a composite perovskite compound precipitate, and, in continuation, a solution of an alkoxide or a hydrolyzable organic metal compound containing a metal element for the improvement of the temperature coefficient (sixth solution) and the slurry of the composite perovskite compound precipitate formed in the primary reaction are fed from separate paths to the later stage of the static stirring-mixing apparatus to carry out the secondary reaction.

7. The manufacturing method described in Claim 6, in which the metal element required for semiconductor formation is at least one metal element selected from niobium, tantalum, bismuth, antimony, yttrium, thorium, tungsten, tantalum, and cerium.

8. The manufacturing method described in Claim 7, in which the metal element for the improvement of the temperature coefficient is at least one metal element selected from manganese, iron, copper, and chromium.

### Detailed explanation of the invention

[0001]

#### Industrial application field

The present invention relates to a method for the manufacture of a raw material powder for electronic ceramics. More specifically, it relates to a method for the manufacture of a raw material powder for electronic ceramics with well-distributed particle diameters, closeness to the so-called monodispersion, high surface activity, and easy sintering characteristics.

[0002]

Prior art

One example of a method to obtain a raw material powder for electronic ceramics by the wet process synthesis method is described in Japanese Kokai Patent Application No. Sho 59[1984]-128263, proposed by the present inventors. This method for the manufacture of the raw material powder for ceramics consists of the following three processes. First of all, in the first process, an aqueous solution of carbon dioxide or sodium carbonate, ammonium carbonate or other soluble carbonates are added to an aqueous solution of a nitrate or chloride containing at least one of barium, strontium, calcium, magnesium, etc., as constituent elements in a first tank. The pH is adjusted to 7-10 to precipitate the carbonate. In the second tank, in an aqueous solution of a nitrate or chloride containing at least one of titanium, zirconium or tin as constituent elements, sodium hydroxide, potassium hydroxide or another caustic alkali is added to pH 7-10 to cause precipitation as a hydroxide. In the second process, a slurry containing a variety of precipitates obtained in the first process is mixed. After filtration, it is washed with water and dried. In the third process, the resulting mixed precipitate is calcined and pulverized. In addition, methods for the manufacture of raw material powder for ceramics by the wet process method have been proposed in Japanese Kokai Patent Applications Nos. Sho 59[1984]-195574, Sho 59[1984]-195576, etc. In any of the methods mentioned previously, in which, for example, barium is used, a process is included in which a solution containing a precipitating agent, such as sodium carbonate or the like, is added to a solution of barium chloride so that the pH is adjusted to 7-10 to cause precipitation as a carbonate.

[0003]

Problems to be solved by the invention

In the processes of the conventional methods described previously, during contacting of the precipitating agent in the solution containing constituent components of the ceramic material, the ratio of the volume of the solution of the precipitating agent with respect to the total volume of the solution containing constituent components of the ceramic material is very small. Therefore, in the case of contacting with the solution containing the precipitating agent, the pH of said contacting portion of the solution containing constituent components of the ceramic material will be very high. The pH of the noncontacting portions will be in a state exhibiting the value as such. The local pH values will be different to a large extent. Furthermore, with the progress of the addition of the solution containing the precipitating agent to the solution containing constituent components of the ceramic material, the pH inside the reaction tank will change gradually. Therefore, a variety of products, in the end, precursors-intermediate-products ceramic compounds [sic], are formed in sequence in a time series in stages of the reaction. This

is undesirable since powder characteristics of the products formed in the initial stage and the products formed in the final stage are different. Furthermore, if the range of pH in which chemical species themselves are stable in the various products is deviated from, dissolution will occur again or chemical species of different constitution ratios may be formed. Since the pH of the mutual contacting portion and the pH of the solution as a whole vary to a large extent in the stage of the addition of the solution containing the precipitating agent to the solution containing constituent components of the ceramic material, situations are poor in which the precipitate concentration is decreased owing to the dispersion of the once formed product into the reaction solution as a whole due to stirring, or the growth of particles occurs owing to redissolution due to a reduction in the pH of the precipitate interface. Variations in particle diameters occur owing to the elapse of time in the formation stage, or the reformation of products due to deviations in constitution ratios occur.

[0004]

Furthermore, a method has been considered in which composite perovskite compound particles of certain particle diameters are manufactured beforehand as seed particles, if necessary, said seed particles are grown, and particles with relatively larger particle diameters are manufactured. This is a method in which, after the dispersion of the seed particles in a solvent consisting of water or the like, particles larger than said seed particles are grown by the addition of a hydrolyzable organic metal compound. However, if said seed particles are added to a solvent consisting of water or the like, the current situations are that said seed particles undergo agglomeration, adhere onto the walls of the reaction vessel walls or settle to the bottom of the reaction vessel, and said seed particles do not grow at all.

[0005]

On the other hand, in a method similar to the conventional wet process synthesis method, that is, in the case of the slow addition of a mixed solution of alkoxides or a composite alkoxide solution of the metal element constituting B (solution B) to a solution containing an alkali, hydroxide of the alkaline-earth metal element constituting A, and seed particles of a composite perovskite compound at 80-95°C (solution A), since the ratio of solution B to the total solution A is very small in the initial stage, the concentration of the ceramic raw material powder formed is low. While the redissolution and deposition are repeated until the precipitate formed is insoluble, it passes through a process in which an insoluble precipitate is formed. Thus, with the progress of the reaction, residual ions in the reaction solution will decrease with the reaction time. The repetition of the redissolution and deposition of the precipitate formed will increase. The diameters of the resulting precipitate particles will be larger than those in the initial stage.

Therefore, in such a method, a time series change in the diameters of the resulting precipitate particles will occur. It is impossible to manufacture a raw material powder with a narrow particle size distribution. Furthermore, since seed particles are added to a strongly alkaline aqueous solution, the strong agglomeration of the seed particles themselves occurs. There is a problem in the dispersion of the seed particles. It is difficult to say that the conventional wet process synthesis method is a good method.

[0006]

In view of these things, the objective of the present invention is to provide a manufacturing method for the synthesis of a product with the uniform dispersion of additives in minute quantities, without variations in particle diameters of formed particles due to redissolution-recrystallization of the product during the reaction process and without discrepancies in constitution ratios, during the formation of the ceramic raw material powder.

[0007]

Means to solve the problems

As a result of zealous investigations in order to achieve the previously described objective, the present inventors discovered that, by feeding a solution of a hydroxide of a metal element constituting A, a solution of a base, and a reaction solution obtained by the dispersion of an alkoxide of a metal element constituting B or a hydrolyzable organic metal compound and seed particles separately at specific ratios to a static mixing-stirring apparatus with metering pumps and allowing them to react, a raw material powder for electronic ceramics relatively larger than the seed particles, and having extremely well-distributed particle diameters, high surface activity, and good sintering characteristics can be manufactured at a low cost and good efficiency. The present invention has thus been accomplished.

[0008]

In other words, the present invention provides (1) a method for the manufacture of a raw material powder for electronic ceramics characterized by the fact that a heated solution obtained by the dispersion of seed particles of a composite perovskite compound of the general formula  $ABO_3$  (in this formula, A is at least one metal element selected from divalent alkaline-earth metals, and B is at least one metal element selected from tetravalent metal elements) (first solution), a heated solution of the hydroxide of the alkaline-earth metal constituting A (second solution), a heated solution of a base (third solution), and a solution of an alkoxide of metal element constituting B or a hydrolyzable organic metal compound containing the element constituting B (fourth solution) are fed at specific molar ratios from separate paths to a static

stirring-mixing apparatus having no moving parts, and contacting and stirring-mixing of the previously mentioned first, second, third and fourth solutions are carried out to the confluence point, at which said solutions are fed to the previously mentioned static stirring-mixing apparatus, to obtain a composite perovskite compound powder shown by the general formula  $ABO_3$  (the various symbols in this formula have the same definitions as those given previously); and (2) a method for the manufacture of a raw material powder for electronic ceramics characterized by the fact that the first, second, third and fourth solutions described in (1) as well as a solution an alkoxide or a hydrolyzable organic metal compound containing a metal element required for semiconductor formation (fifth solution) are fed separately to a static stirring-mixing apparatus having no moving parts to carry out the primary reaction for the formation of a composite perovskite compound precipitate, and, in continuation, a solution of an alkoxide or a hydrolyzable organic metal compound containing a metal element for the improvement of the temperature coefficient (sixth solution) and the composite perovskite compound precipitate slurry formed in the primary reaction are fed from separate paths to the later stage of the static stirring-mixing apparatus to carry out the secondary reaction.

[0009]

In the present invention, as divalent alkaline-earth metals represented by A, for example, barium, calcium, strontium, magnesium, and so on can be mentioned. As tetravalent metal elements represented by B, titanium, zirconium, tin, and so on can be mentioned. The first solution is water or a system formed by mixing with an alcohol. It is a solution containing an alkali with the pH adjusted to above 10, preferably about 14, in which are dispersed seed particles of the composite perovskite compound described previously are dispersed. As the alcohols, methanol, ethanol, isopropanol, sec-butanol, and other alcohols with boiling points below 100°C are appropriate. The concentration of the seed particles can be up to 30 wt% with respect to the composite perovskite compound to be formed. However, it is appropriate at 1 wt% to more than approximately 10 wt%. The heating temperature of the solution is preferably 80-95°C.

[0010]

The second solution is a heated solution of hydroxides of the alkaline-earth metal constituting A. As the hydroxides that can be used, barium hydroxide, strontium hydroxide, magnesium hydroxide, and calcium hydroxide can be mentioned. A solution obtained by the dissolution of the hydroxide in a solvent for a relative molar ratio of 1.00-1.03 with respect to the element constituting B is used. As the solvent, distilled water can be used. The heating temperature of the solution is preferably 80-95°C.



[0011]

The third solution is a heated solution of a base. As the bases that can be used, sodium hydroxide, potassium hydroxide, lithium hydroxide, ammonium hydroxide, organic amines and so on can be mentioned. These can be used alone or as a mixture of two or more. As said organic amines, for example, methylamine, dimethylamine, trimethylamine, ethylamine or other aliphatic amines; o-, m- or p-toluidine, N,N-dimethylbenzylamine or other aromatic amines can be mentioned as typical examples. The base is used at molar ratio of 1-4 with respect to the element constituting B. As the solvents, pure water or distilled water can be mentioned. The heating temperature of the solution is preferably 80-95°C.

[0012]

The fourth solution is a solution of alkoxides of the metal element constituting B or hydrolyzable organic metal compounds containing the metal element constituting B. As the alkoxides of the metal element constituting B that can be used, for example, methoxide, ethoxide, isopropoxide, butoxide and so on of said metal elements can be mentioned. Furthermore, said alkoxides may be mixtures of these or composite alkoxides. As the metal element constituting B, in the case of using titanium, titanium alkoxides, titanium isopropoxide, titanium butoxide, titanium ethoxide, titanium dibutoxyditriethanol aminate, dibutoxy(2-hydroxyethylaminoethoxy) titanium and so on can be mentioned. Furthermore, as metal compounds for carrying out composite alkoxide formation, it is advantageous to use zirconium acetate, lanthanum acetate or other acetates that can easily undergo the ester exchange reactions. It is also acceptable to use metal alkoxides capable of composite formation by the utilization of the alcoholysis reaction. In regard to cost, it is advantageous to use acetate. However, it is not to be restricted to this. As hydrolyzable organic metal compounds containing the metal element constituting B, Ti acetyl acetonate, Zr acetyl acetonate, and Sn acetyl acetonate can be mentioned. These alkoxides or hydrolyzable organic metal compounds are dissolved in organic solvents and their concentrations are adjusted to 0.7-0.8 mol/L. As the solvents, isopropyl alcohol, ethanol, methanol, sec-butanol, or other alcohols as organic solvents with boiling points below 100°C are appropriate.

[0013]

The fifth solution is a solution of alkoxides or hydrolyzable organic metal compounds containing the metal element required for semiconductor formation. The metal element required for semiconductor formation is at least one metal element selected preferably from niobium, tantalum, bismuth, antimony, yttrium, thorium, tungsten, tantalum, cerium or other rare-earth elements. As said alkoxides, methoxide, ethoxide, isopropoxide, butoxide and so on of said metal

elements can be mentioned. Furthermore, said alkoxides may be mixtures of these or composite alkoxides. As said hydrolyzable organic metal compounds, acetyl acetonate compounds of the metals mentioned previously can be mentioned. These alkoxides or hydrolyzable organic metal compounds are dissolved in organic solvents and their concentrations are adjusted to 0.05-0.1 mol/L. As the solvents, isopropyl alcohol, ethanol, methanol, sec-butanol, or other alcohols as organic solvents with boiling points below 100°C are appropriate.

[0014]

The sixth solution is a solution of alkoxides or hydrolyzable organic metal compounds containing the metal element for improvement of the temperature coefficient. The metal element for the improvement of the temperature coefficient is at least one metal element selected preferably from manganese, iron, copper, and chromium. As said alkoxides, methoxide, ethoxide, isopropoxide, butoxide and so on of said metal elements can be mentioned. Furthermore, said alkoxides may be mixtures of these or composite alkoxides. As said hydrolyzable organic metal compounds, acetyl acetonate compounds of these elements can be mentioned. These alkoxides or hydrolyzable organic metal compounds are dissolved in organic solvents and their concentrations are adjusted to 0.05-0.1 mol/L. As the solvents, isopropyl alcohol, ethanol, methanol, sec-butanol, or other alcohols as organic solvents with boiling points below 100°C are appropriate.

[0015]

In one of the embodiments of the present invention, the first, second, third and fourth solutions are fed at specific molar ratios from separate paths to a static stirring-mixing apparatus having no moving parts, and contacting and stirring-mixing of these solutions are carried out to the confluence point, at which said solutions are fed to the previously mentioned static stirring-mixing apparatus to manufacture a composite perovskite compound powder. Molar ratios of the solutions fed to the static stirring-mixing apparatus are preferably such that  $A:B:base = 1:1:(1-4)$ .

[0016]

The apparatus example for the implementation of the present embodiment will be explained on the basis of Figure 1 in the following. In Figure 1, (1) through (4) are tanks for the storage of the first solution, the second solution, the third solution, and the fourth solution, respectively. Pipes (5) through (8) are connected to the various tanks. With metering liquid-delivering pumps (9) through (12) and from pipes (13) through (16), the first solution through the fourth solution mentioned previously are fed separately at specific molar ratios in a

quantitative manner via a fluid mixer (17) to a static stirring-mixing apparatus (18) having no moving parts. At this stage, the first solution through the fourth solution undergo contacting and reaction to synthesize the ceramic raw material powder. By feeding the four types of reaction solutions in a quantitative manner with metering pumps (9) through (12), the reaction concentration at the reaction interface is kept constant from the beginning to the end of the reaction. The ceramic raw material powder precipitate formed does not undergo a time series change and is formed at a constant amount little by little. No difference is observed in powder characteristics between the ceramic raw material powder formed in the initial stage and the ceramic raw material powder formed in the later stage. Thus, stable manufacture of the ceramic raw material powder precipitate is made possible. The product obtained is fed from the pipe (19) to the product storage tank (20).

[0017]

Preferably, means for dividing the mixed fluid into two by the fixation of, for example, twisting impellers, are installed in  $n$  stages inside the static mixing-stirring apparatus. In this case, the ceramic raw material powder precipitate slurry is divided into  $2n$  units, and mixed and stirred. For example, for a static mixing-stirring apparatus having 27 stages of twisting impellers, division into  $2^{27} = 1.3 \times 10^8$  units is conducted and uniform mixing-stirring is made possible.

[0018]

Furthermore, in another embodiment of the present invention, the first, second, third and fourth solutions described in (1), as well as the fifth solution, are fed separately to a static stirring-mixing apparatus having no moving parts to carry out the primary reaction for the formation of a composite perovskite compound precipitate, and, in continuation, the sixth solution and the composite perovskite compound precipitate slurry formed in the primary reaction are fed from separate paths to the later stage of the static stirring-mixing apparatus to carry out the secondary reaction, to manufacture a raw material powder for electronic ceramics. This manufacture can be conducted by using, for example, the same apparatus, as shown in Figure 2, having a static stirring-mixing apparatus as that described previously. In the apparatus of Figure 2, tanks ((1'), (2'), (3'), (4'), (26), and (30)) for the storage of the first solution, the second solution, the third solution, the fourth solution, the fifth solution, and the sixth solution, respectively, are installed. Pipes ((5') through (8'), (27), and (21)) are connected to the various tanks. With metering liquid-delivering pumps ((9') through (12') and (28)) and from the connected pipes ((13') through (16') and (29)), the first solution through the fifth solution are fed separately at specific molar ratios of the various solution components in a quantitative manner via a fluid mixer (17') to a static stirring-mixing apparatus (18') having no moving parts. The

slurry obtained is fed from the pipe (19') via a fluid mixer (23) to a static stirring-mixing apparatus (24) having no moving parts. On the other hand, the sixth solution, separate from the various solutions mentioned previously, is fed with a metering liquid-delivering pump (22) from the connected pipe (21) in a quantitative manner via a fluid mixer (23) to a static stirring-mixing apparatus (24) having no moving parts. The product obtained is fed from the pipe (25) to the product storage tank (20'). In the present apparatus, a separate precipitate can be synthesized in continuation by using the precipitate formed in the former process. Uniform mixing and dispersion are made possible. A ceramic raw material powder more stable than that by the conventional method can be manufactured.

[0019]

#### Application examples

The present invention will be further explained in detail with a reference example, application examples, and a comparative example in the following. However, the present invention is not to be restricted to these.

#### Reference Example 1

##### Production of seed particles

The metal elements constituting A and sodium hydroxide were weighed accurately according to Table 1. They were dissolved in 1000 cc of pure water heated at 90°C to prepare solution A. The metal element isopropoxide constituting B was weighed accurately according to Table 1. It was transferred into a vessel to which isopropanol (to be simply called IPA hereafter) had been introduced beforehand. Furthermore, more IPA was added to a total amount of 1000 cc to prepare solution B. Solution A and solution B were fed at 300 cc/min each using metering liquid-delivering pumps to a static stirring-mixing apparatus having 10 stages of twisting impellers, to cause the reaction for the formation of the perovskite compound for use as seed particles. The reaction solutions were kept at 90°C. While they were being passed through the static stirring-mixing apparatus, ripening was carried out for 3 h. After ripening, the compound precipitate was recovered and washed with water to remove  $\text{Na}^+$  to obtain seed particles. The seed particles after the removal of  $\text{Na}^+$  were dispersed in an organic solvent adjusted to pH 9 using ammonia to yield the first solution. The concentration of the seed particles was adjusted each time according to the intended use.

[0020]

Table 1

Blended ratios for the synthesis of seed particles

① 種粒子の種類	Ba	Sr	Ti	Zr	NaOH
② BT粒子	1.00	0.00	1.00	0.00	4.00
③ BST粒子	0.70	0.30	1.00	0.00	4.00
④ BTZ粒子	1.00	0.00	0.90	0.10	4.00

The figures in the table are in molar ratios.

Key: 1      Type of seed particles  
 2      BT particles  
 3      BST particles  
 4      BTZ particles

[0021]

#### Application Examples 1 through 4

Various solutions were prepared according to Table 2. Hydroxides of alkaline-earth metal elements constituting A were weighed accurately. They were dissolved in 1000 cc of pure water heated at 90°C to prepare the second solution. Alkoxides of the metal elements constituting B were weighed accurately and transferred into vessels to which IPA had been introduced beforehand. Furthermore, more IPA was added to a volume of 1000 cc to prepare the fourth solution. Sodium hydroxide was dissolved in 1000 cc of pure water heated at 90°C to prepare the third solution. The first solution through the fourth solution prepared were fed at 250 cc/min each using metering liquid-delivering pumps to a static stirring-mixing apparatus having 10 stages of twisting impellers, to cause the reaction for the synthesis of the desired perovskite compound precipitate. The resulting compound precipitate was recovered and washed with water to remove  $\text{Na}^+$ . The washed precipitate was subjected to dewatering of the precipitate compound powder using Ekinen [transliteration] and dried at 60°C to obtain a raw material powder.

[0022]

Table 2  
Test blending specifications

① 実施例番号	1	2	3	4
水酸化バリウム ②	0.2 mol	0.14mol	0.02mol	0.20mol
③ 水酸化ストロンチウム	0.00	0.06	0.00	0.00
Ti(OC <sub>3</sub> H <sub>7</sub> ) <sub>4</sub>	0.20	0.20	0.18	0.20
Zr(OC <sub>3</sub> H <sub>7</sub> ) <sub>4</sub>	0.00	0.00	0.02	0.00
水酸化ナトリウム ④	32 gr	32 gr	32 gr	32 gr
種粒子濃度 ⑤	5.0%	5.0%	5.0%	なし ⑥

Key: 1 Application Example No.  
 2 Barium hydroxide  
 3 Strontium hydroxide  
 4 Sodium hydroxide  
 5 Seed particle concentration  
 6 None

[0023]

#### Comparative Example 1

With the same composition as Application Example 4, ammonium carbonate was added dropwise to barium chloride and the pH was adjusted to 9-9.5 to synthesize a precipitate of barium carbonate. Furthermore, aqueous H<sub>2</sub>O<sub>2</sub> and ammonia solutions were added dropwise to an aqueous titanium tetrachloride solution, and the pH was adjusted to 9-9.5 to obtain a precipitate of a titanium compound. The various precipitates were mixed and water washing was carried out by filtration and dewatering. It was dried and calcined at 1000°C to obtain a BaTiO<sub>3</sub> powder. This comparative example was conducted for the comparison of uniformity with that by the conventional wet process synthesis method.

[0024]

Analytical results of the synthesized powder

The XRD analyses of the powders obtained in Application Examples 1 through 4 and the comparative example were conducted and the results are shown in Table 3. Furthermore, for the powders obtained in the comparative example and Application Example 2, molar ratio analyses were carried out randomly for 10 points with a spot diameter of 1 μm using a transmission

electron microscope. The results are shown in Tables 4 and 5. Moreover, for Application Examples 1 through 4, measurements of the specific surface (SS) were conducted. The results of particle diameters calculated from these, average particle diameters determined from TEM photographs, and standard deviations (3 sigma) are shown in Table 3.

[0025]

Table 3  
Evaluation results of synthesized powders

EXP. NO	XRD分析 結果 ①	SS (m <sup>2</sup> /gr)	SS径 ( $\mu$ m)②	TEM径 ( $\mu$ m)③	標準偏差 (3 $\sigma$ )④
1	Perovskite	6.67	0.15	0.13	0.03
2	Perovskite	6.67	0.15	0.14	0.02
3	Perovskite	8.33	0.12	0.12	0.03
4	Perovskite	14.3	0.07	0.06	0.01
⑥ 比較例	Perovskite	⑤ -	-	-	-
⑦ 種粒子 BT粒子	Perovskite	16.7	0.06	0.07	0.01

Key: 1 XRD analytical results  
 2 SS diameter  
 3 TEM diameter  
 4 Standard deviation  
 5 Perovskite  
 6 Comparative Example  
 7 Seed particles, BT particles

[0026]

As seen from the results in Table 3, the particle diameter of the powder (Application Example 4) synthesized without the seed particles had the same particle diameter as that of the seed particles. In contrast to this, it was confirmed that the powders synthesized with the seed particles had particle diameters 2 to 3 times that of the seed particles. Also shown from these results, it is clear that this is an effective method for the manufacture of particles with larger particle diameters than that of the original particles by the deposition of the newly synthesized powder on of the seed particles. Furthermore, the particle diameters calculated from SS and the particle diameters obtained from the TEM observations were in agreement. Moreover, the fact that 3 sigma was small shows that the distribution of particle diameters was narrow. In addition, it is seen from the molar ratio analytical results in Tables 4 and 5 that the molar ratio discrepancies were large at various analytical locations for the powders obtained by the conventional method. In contrast to this, as the powders obtained by the method of the present

invention, ceramic raw material powders with particles at 1 to 1 [correspondence] to the theoretical values were obtained. The superiority of the present invention can be clearly seen.

[0027]

Table 4

Molar ratio analytical results of powders of the present invention

① 分析地点	Ba	Sr	Tl
1	0.700	0.299	1.001
2	0.698	0.300	0.998
3	0.706	0.294	1.003
4	0.695	0.305	1.000
5	0.700	0.297	0.997
6	0.699	0.297	1.004
7	0.694	0.305	0.999
8	0.704	0.299	1.003
9	0.694	0.301	0.995
10	0.708	0.295	1.008
② 理論値	0.700	0.300	1.000

Key: 1 Analytical location  
2 Theoretical value



[0028]

Table V  
Molar ratio analytical results of powders of the conventional method

① 分析地点	Ba	Ti
1	0.00	2.00
2	1.45	0.55
3	1.40	0.60
4	0.80	1.20
5	0.60	1.40
6	1.30	0.70
7	1.10	0.90
8	0.90	1.10
9	0.85	1.15
10	1.25	0.75
② 理論値	1.00	1.00

Key: 1 Analytical location  
2 Theoretical value

[0029]

#### Effects of the invention

According to the present invention, sufficiently dispersed, novel composite perovskite is formed on the surface of seed particles. A composite perovskite compound precipitate having a particle diameter larger than that of the seed particles and being close to monodispersion can be formed. The conventional problems can be solved. Furthermore, by using a static mixing-stirring apparatus, especially a static mixing-stirring apparatus installed with several stages of twisting impellers, in the present invention, the mixing-stirring efficiency is improved to a large extent in comparison to the conventional case, and uniform dispersion is made possible. In addition, the static mixing-stirring apparatus is very small in comparison to the conventional stirring reaction apparatus. A small space of the reactor is sufficient. The multiple reactions can also be carried out continuously by simply connecting static mixing-stirring apparatuses. As shown from the explanation above, according to the present invention, a method is provided by which a raw material powder for electronic ceramics that has particles larger than the seed particles, has extremely well distributed particle diameters, has a high surface activity, and has good sintering characteristics can be manufactured at a low cost in an efficient manner.

### Brief description of the figures

Figure 1 is an illustrative diagram for an apparatus that can be used in the first embodiment of the present invention.

Figure 2 is an illustrative diagram for an apparatus that can be used in the second embodiment of the present invention.

### Explanation of symbols

1-4, 1'-4'	Storage tanks of the first solution, the second solution, the third solution, and the fourth solution
5-8, 5'-8'	Pipes
9-12, 9'-12'	Metering liquid-delivering pumps
13-16, 13'-16'	Pipes
17, 17'	Fluid mixers
18, 18'	Static mixing-stirring apparatuses
19, 19'	Pipes
20, 20'	Storage tanks of products
21	Pipe
22	Metering liquid-delivering pump
23	Fluid mixer
24	Static mixing-stirring apparatus
25	Pipe
26	Storage tank for the fifth solution
27	Pipe
28	Metering liquid-delivering pump
29	Pipe
30	Storage tank for the sixth solution

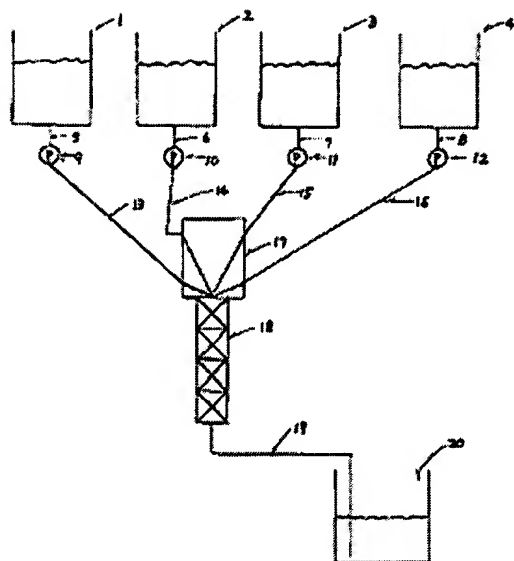


Figure 1

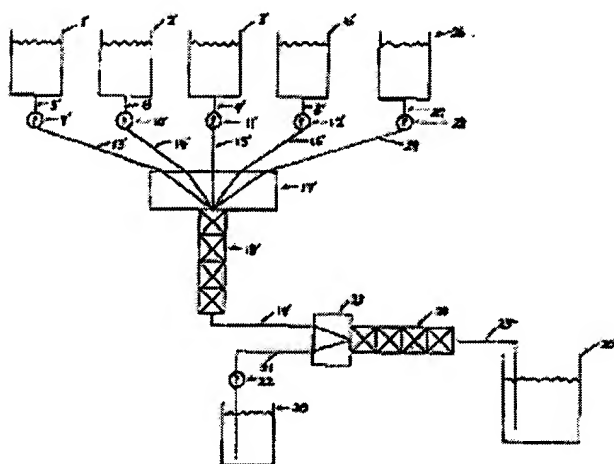


Figure 2